Preparation and sensitive properties of block copolymer humidity sensitive materials with nanostructure

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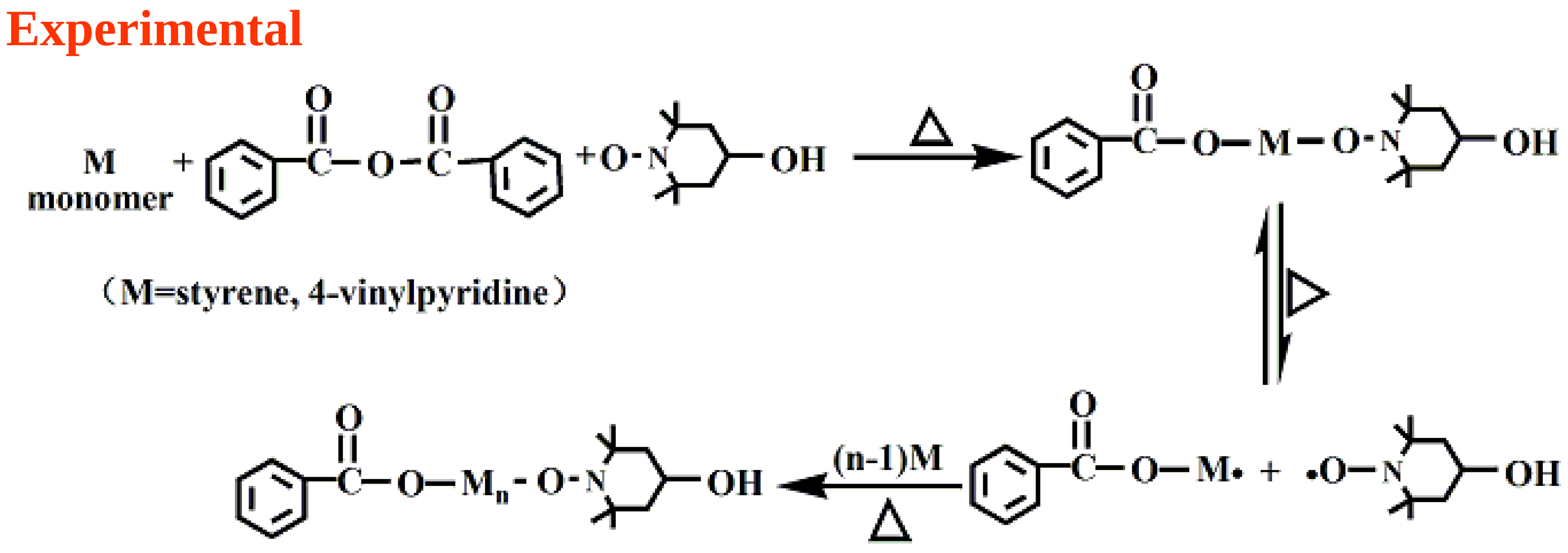
Abstract

Nanostructured thin film impedance-type humidity sensors have been prepared by sulfonation of phase separated styrene-4-vinylpyridine block copolymer. Humidity sensing properties of the copolymer based sensors were investigated at room temperature, and the sensing mechanism was explored. As-prepared sensor exhibited nanoporous structure, and revealed very high sensitivity towards relative humidity (RH) (impedance change of three orders of magnitude in the range of 40-90%RH). Moreover, the nanostructure endowed the sensor with fast response both for adsorption ($t_{90\%}$ of 10 s) and desorption ($t_{90\%}$ of 13 s), suggesting its potentials in the applications of fast and sensitive detection of humidity.

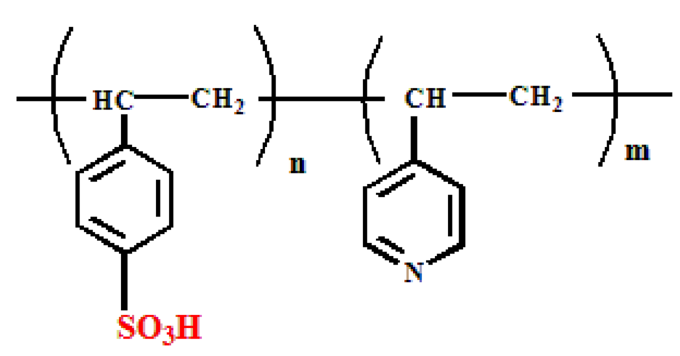
Experimental



Scheme 1 THEMPO-mediated living free-radical polymerization of styrene and 4-vinylpyridine.

Sample	M_w	M_w/M_n	PS in copolymer (mol%)
PS-b-P4VP	31918	1.27	65.2%

Table 1 Molecular weights and compositions of PS-b-P4VP



Scheme 2 Chemical Structure of PS-SO_3H-*b*-P4VP.

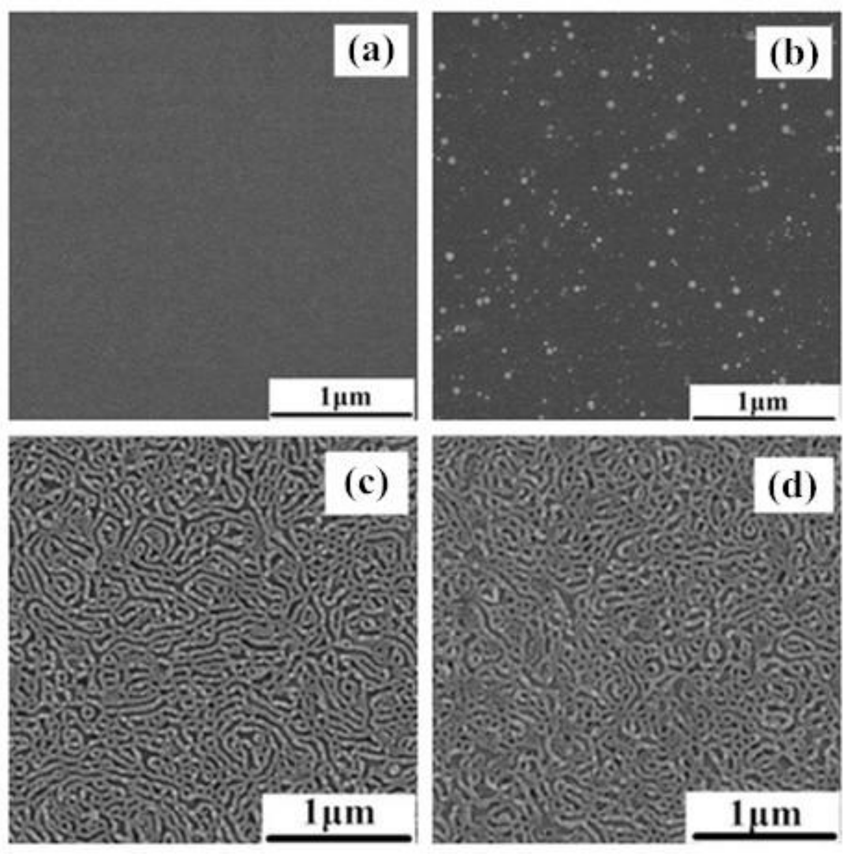


Fig. 1 SEM images of PS-*b*-P4VP before (a) and after (c) phase separation, and sulfonated PS-*b*-P4VP (b, d).

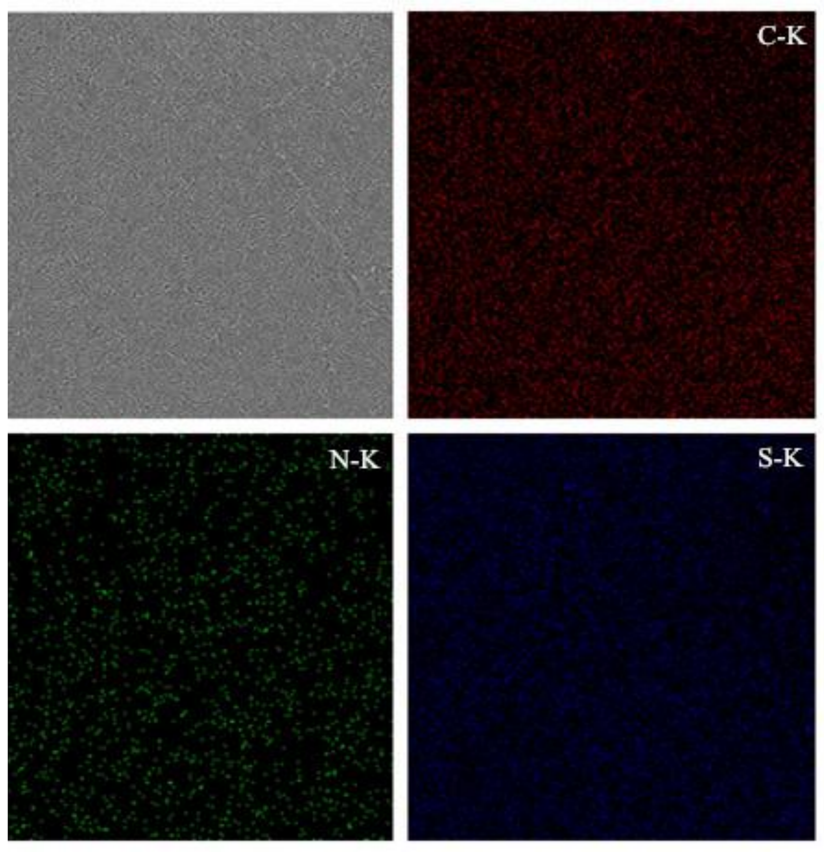


Fig. 2 EDAX mapping of sulfonated PS-*b*-P4VP .

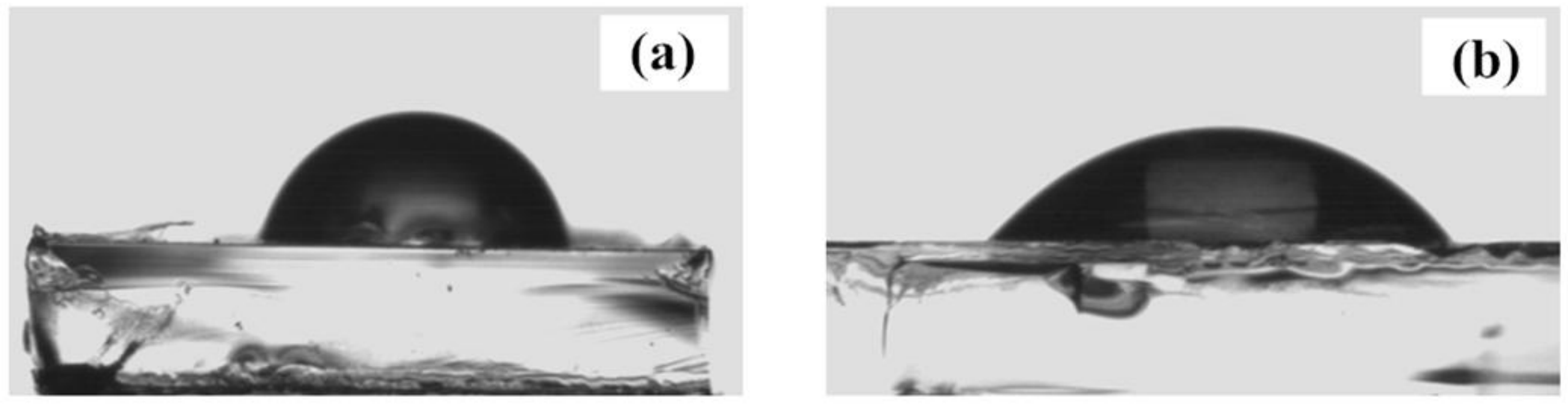


Fig. 3 Photos of contact angle measurement of PS-b-P4VP before (a) and after sulphonation (b) .

Results and discussion

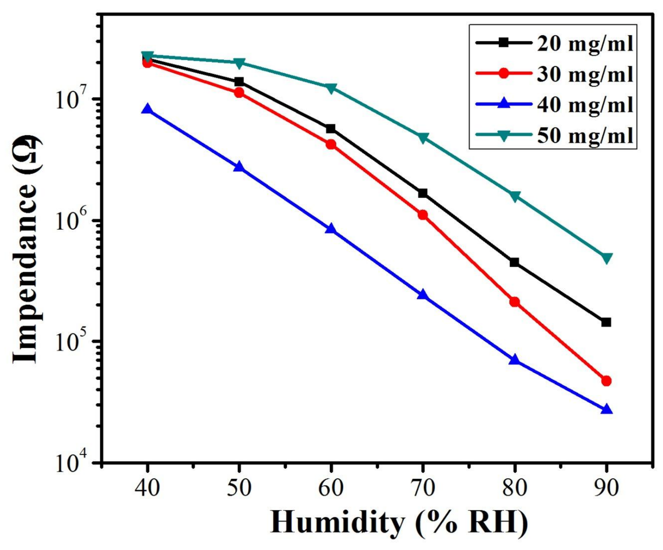


Fig. 4 Effect of concentration of PS-SO_3H-b-P4VP on the humidity sensing properties.

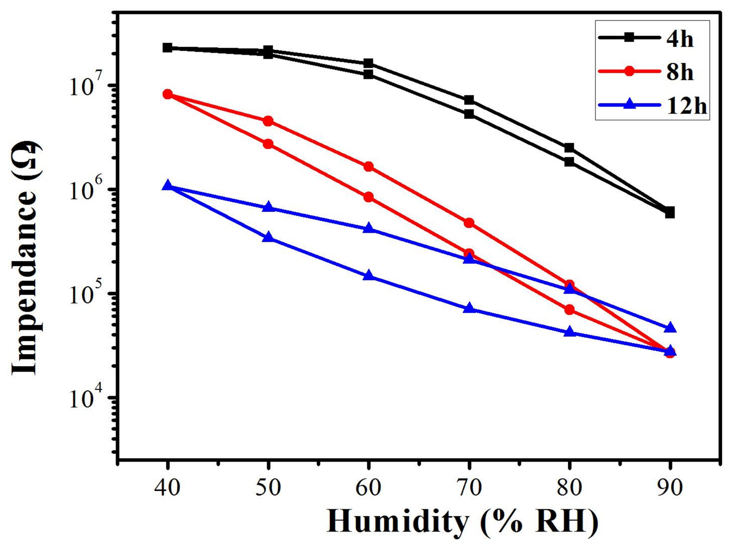


Fig. 5 Effect of sulfonation time of PS-SO_3H-b-P4VP on the humidity sensing properties.

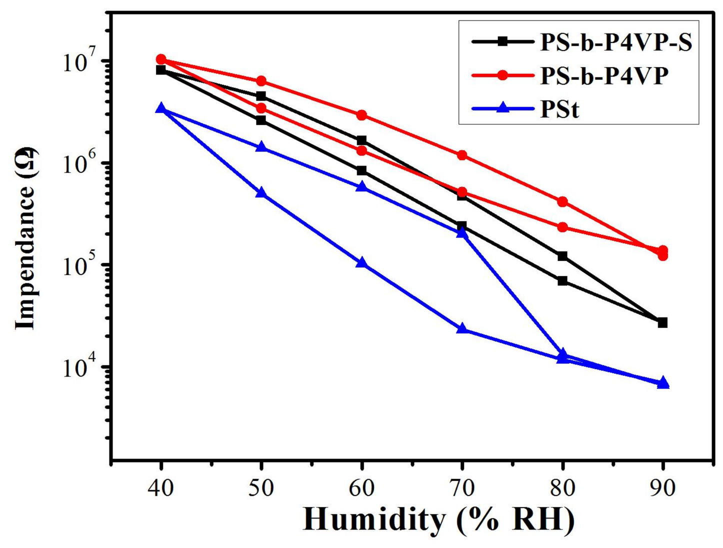


Fig. 6 Humidity sensing properties of sulfonated PSt, and copolymers with and without phase separation.

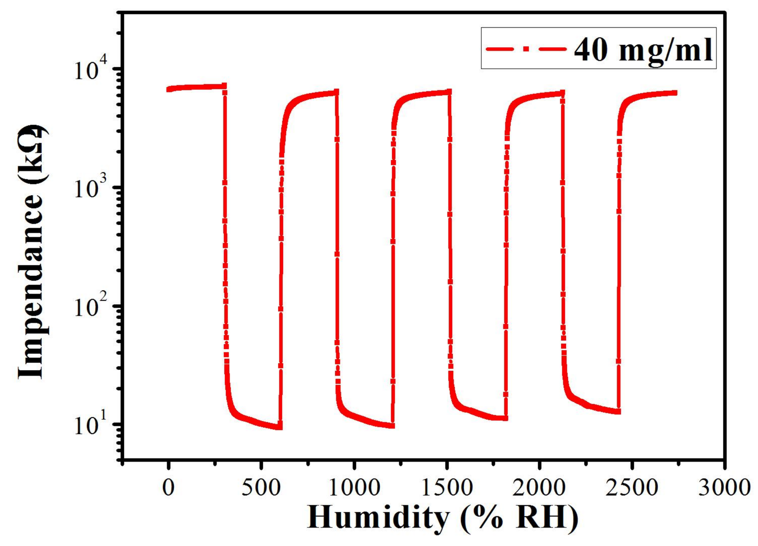


Fig. 7 Response transients of PS-SO_3H-b-P4VP between 33%-98% RH.

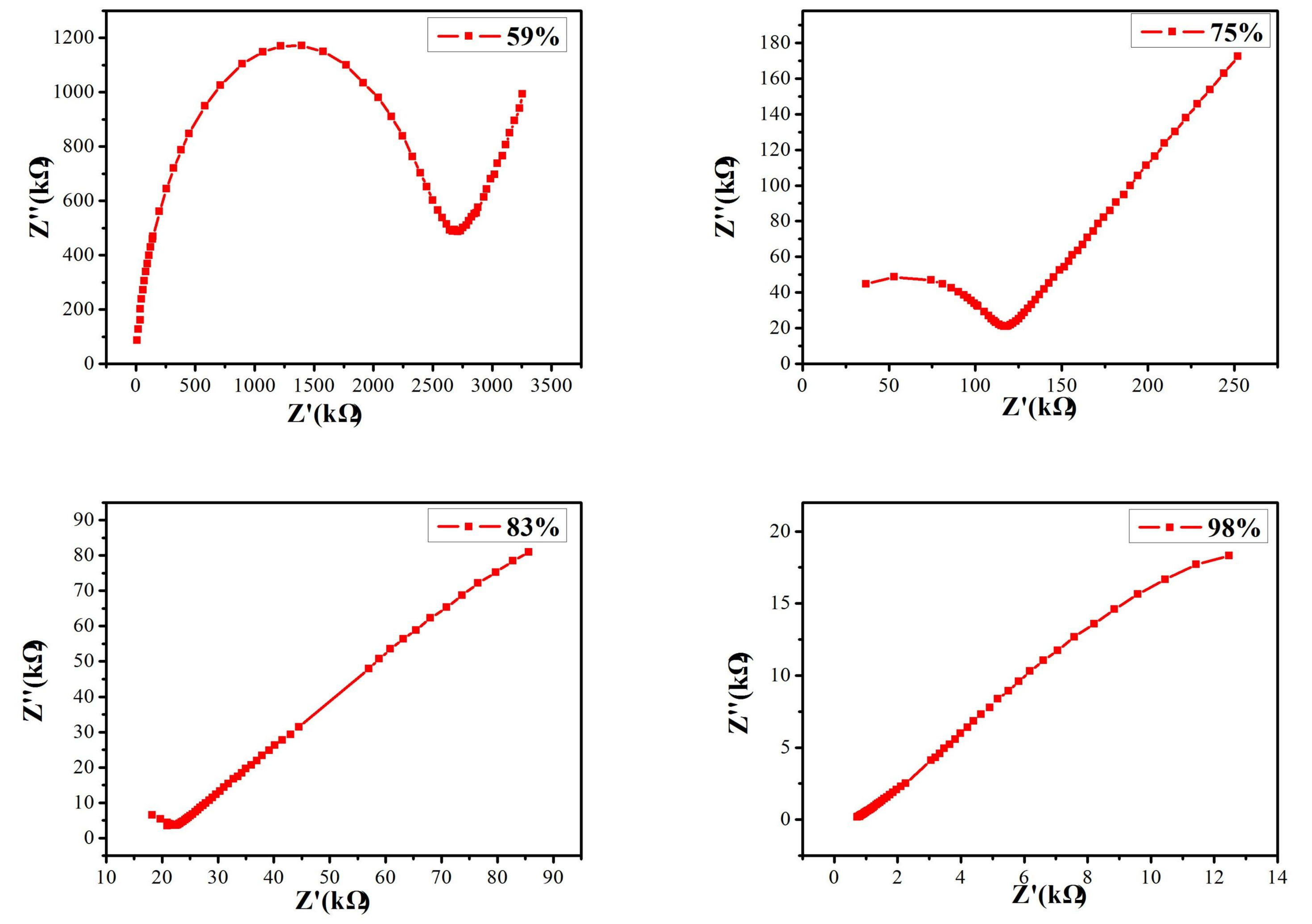


Fig. 8 Nyquist plots of PS-SO_3H-b-P4VP under different RH.

Conclusions

PS-b-P4VP block copolymer was prepared with nitroxide-mediated living polymerization. Selective solvent dissolution induced phase separation resulted in nanoporopus structures in PS-b-P4VP film, and subsequent sulfonation bestowed the copolymer with humidity sensing properties. Thin film humidity sensors based on nanostructured PS-SO_3H-b-P4VP revealed both high sensitivity and short response time for both humidification and desiccation processes. The work provides a new approach for the construction of nanostructured high-performance polymeric humidity sensors.

Acknowledgement

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References

[1] Yin J, Yao X, et al. ACS nano, 2013, 7(11): 9961-9974.

[2] Li Y, Fan K C, et al. Sensors and Actuators B 222 (2016)151-158.